

## **Chapter 7 - Acids, Bases and Salts**

### **Acids and alkalis**

- Theories of acids and bases
- The relative strengths of acids and bases
- Neutralising an acid

### **Formation of salts**

- Methods of preparing soluble salts
- Methods of preparing insoluble salts
- More about salts
- Testing for different salts

### **Crystal hydrates**

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### **Solubility of salts in water**

- Calculating solubility
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### **Titration**

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### **Additional questions**

## Acids and alkalis

All the substances shown in Figure 7.1 contain an **acid** of one sort or another. Acids are certainly all around us. What properties do these substances have which make you think that they are acids or contain acids?

The word acid means 'sour' and all acids possess this property. They are also:

- soluble in water
- corrosive.

**Alkalis** are very different from acids. They are the chemical 'opposite' of acids.

- They will remove the sharp taste from an acid.
- They have a soapy feel.

Some common alkaline substances are shown in Figure 7.2.

It would be too dangerous to taste a liquid to find out if it was acidic. Chemists use substances called **indicators** which change colour when they are added to acids or alkalis. Many indicators are dyes which have been extracted from natural sources. For example, litmus is a purple dye which has been extracted from lichens. Litmus turns red when it is added to an acid and turns blue when added to an alkali. Some other indicators are shown in Table 7.1, along with the colours they turn in acids and alkalis.

Table 7.1 Indicators and their colours in acid and alkaline solution.

Indicator	Colour in acid solution	Colour in alkaline solution
Blue litmus	Red	Blue
Methyl orange	Pink	Yellow
Methyl red	Red	Yellow
Phenolphthalein	Colourless	Pink
Red litmus	Red	Blue

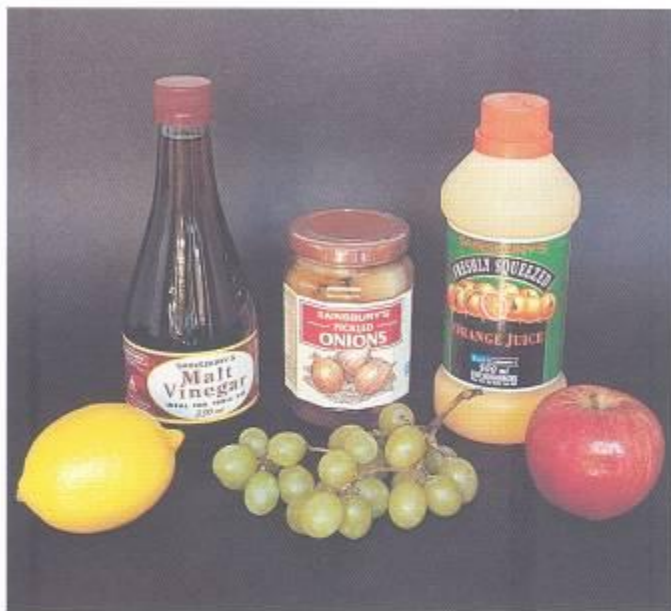


Figure 7.1 What do all these foods have in common?



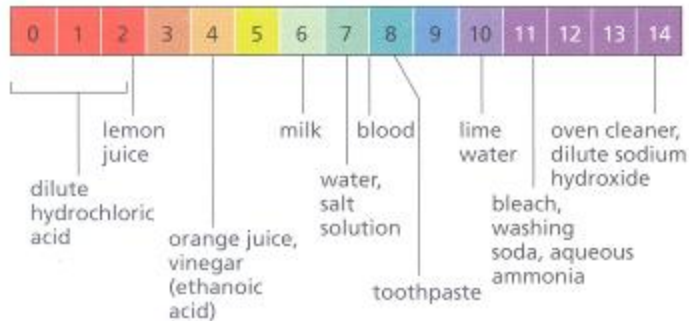
Figure 7.2 Some common alkaline substances.

These indicators tell chemists whether a substance is acid or alkaline (Figure 7.3). To obtain an idea of how acidic or alkaline a substance is, we use another indicator known as a **universal indicator**. This indicator is a mixture of many other indicators. The colour shown by this indicator can be matched against a **pH scale**. The pH scale was developed by a Scandinavian chemist called Soren Sorenson, who was employed by the Carlsberg brewery. The pH scale runs from below 0 to 14. A substance

with a pH of less than 7 is an acid. One with a pH of greater than 7 is alkaline. One with a pH of 7 is said to be neither acid nor alkaline, that is neutral. Water is the most common example of a neutral substance. Figure 7.4 shows the universal indicator colour range along with everyday substances with their particular pH values.



Figure 7.3 Indicators tell you if a substance is acid or alkaline.



a The pH scale.



b Universal indicator in solution, showing the colour range.

Figure 7.4

Another way in which the pH of a substance can be measured is by using a pH meter (Figure 7.5). The pH electrode is placed into the solution and a pH reading is given on the digital display.

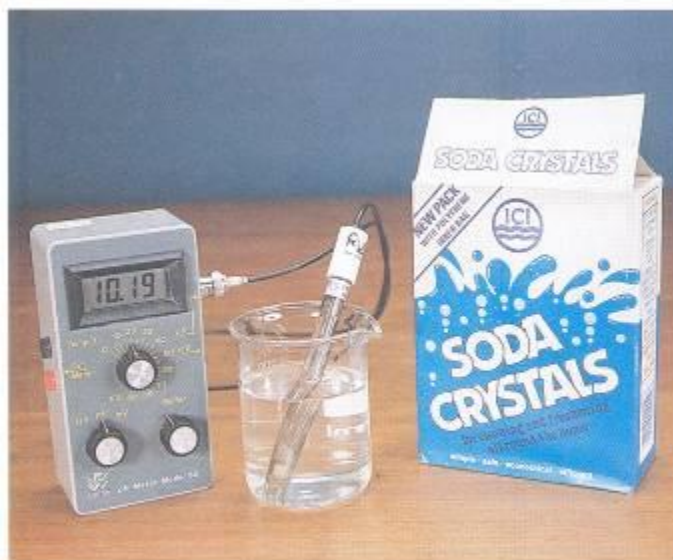


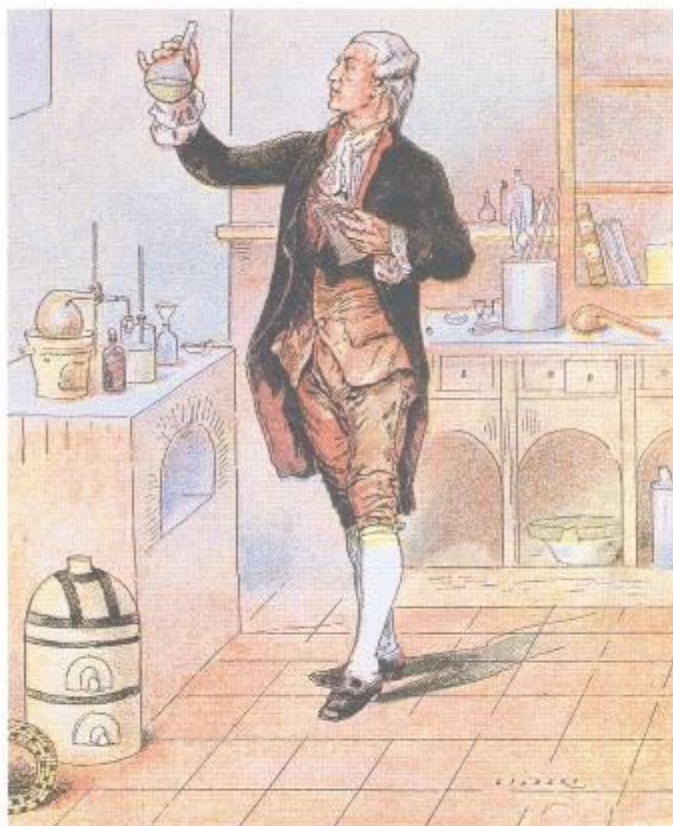
Figure 7.5 A digital pH meter.

## Theories of acids and bases

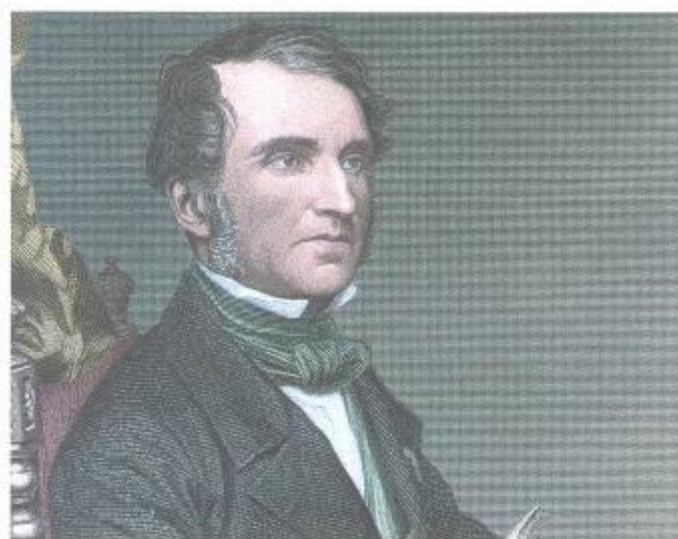
There have been many attempts to define the difference between acids and bases. The first real attempt took place in 1777, when the Frenchman Antoine Lavoisier (Figure 7.6) suggested that acids were substances that contained oxygen.

It was not long after this that the 'hydro-halic' acids (HCl, HBr, and so on) were discovered and they had no oxygen present in them. This produced a modified theory in 1810 when the English chemist Sir Humphry Davy (1778-1829) suggested that all acids contain hydrogen as the important element; however, it was pointed out that there were many hydrogen-containing substances that were not acids. The German chemist Justus von Liebig (Figure 7.7) then made the next useful proposal about acids (1838) when he suggested that acids were substances that can react with metals to produce hydrogen gas.





**Figure 7.6** Antoine Lavoisier (1714–1794) at work in his laboratory.



**Figure 7.7** Justus von Liebig (1803–1873), who defined acids more closely.

This theory was followed in 1884 by the first really comprehensive theory of

acids and bases, produced by the Swedish chemist Svante Arrhenius (1859-1927). He suggested that since these acid solutions were electrolytes (see Chapter 6) their solutions contained many ions. According to Arrhenius' theory, acids produce hydrogen ions ( $\text{H}^+$ ) when they dissolve in water, whereas bases produce hydroxide ions ( $\text{OH}^-$ ).

It was thus recognised that water plays an important part in the acidity of a substance. This led to the suggestion that the hydrogen ion cannot exist alone in aqueous solution. This was prompted by the fact that gaseous hydrogen chloride,  $\text{HCl (g)}$ , is not acidic but when it dissolves in water an acidic solution is produced.

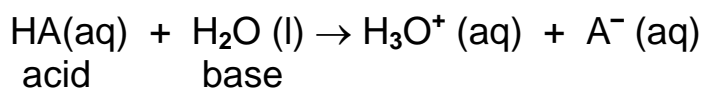
These ideas were rather limiting since they only applied to aqueous solutions. There were situations where acid-base reactions were taking place in solvents other than water, or even in no solvent at all. This problem was addressed in 1923 by the Danish chemist Johannes Brønsted (1879-1947) and the English chemist Thomas Lowry (1874-1936) when they independently proposed a more general definition of acids and bases, and the study of acids and bases took a great step forward. This theory became known as the **Brønsted-Lowry** theory of acids and bases.

### The Brønsted-Lowry theory

This theory defined:

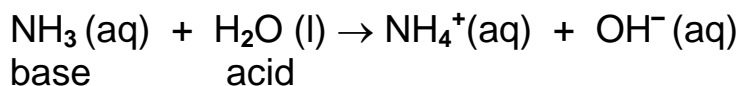
- an acid as an  $\text{H}^+$  ion (or proton) donor
- a base as an  $\text{H}^+$  ion (or proton) acceptor.

The theory explains why a pure acid behaves differently from its aqueous solution, since for an acid to behave as an  $\text{H}^+$  ion donor it must have another sub-stance present to accept the  $\text{H}^+$  ion. So the water, in the aqueous acid solution, is behaving as a Brønsted-Lowry base and accepting an  $\text{H}^+$  ion. Generally:



If a substance can behave both as a Brønsted-Lowry acid and as a Brønsted-Lowry base then it is called **amphoteric**. Water has this ability.

As well as reacting with acids (above) it can also react with Brønsted-Lowry bases such as ammonia in the following way to form the base  $\text{OH}^-$ :



The reaction between hydrogen chloride gas and ammonia can be described as an acid-base reaction under this theory. The hydrogen chloride molecule acts as a proton donor and the ammonia molecule acts as the proton acceptor (Figure 7.8).

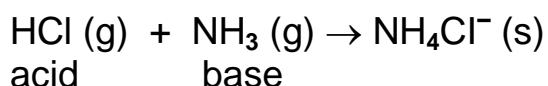


Figure 7.8 The hydrogen chloride molecule (from concentrated hydrochloric acid) acts as a hydrogen ion donor. The ammonia molecule (from concentrated ammonia) acts as a hydrogen ion acceptor.

## The relative strengths of acids and bases

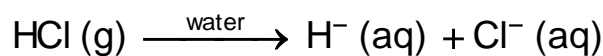
The relative strength of an acid is found by comparing one acid with another. The strength of any acid depends upon how many molecules



dissociate (split up) when the acid is dissolved in water. The relative strength of a base is found by comparing one base with another and is again dependent upon the dissociation of the base in aqueous solution.

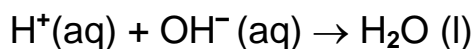
## Strong and weak acids

A typical strong acid is hydrochloric acid. It is formed by dissolving hydrogen chloride gas in water. In hydrochloric acid the ions formed separate completely.



For hydrochloric acid all the hydrogen chloride molecules break up to form  $\text{H}^+$  ions and  $\text{Cl}^-$  ions. Any acid that behaves in this way is termed a **strong acid**. Both sulphuric acid and nitric acid also behave in this way and are therefore also termed strong acids. All these acids have a high concentration of hydrogen ions in solution ( $\text{H}^+ \text{ (aq)}$ ).

When strong acids are neutralised by strong alkalis the following reaction takes place between hydrogen ions and hydroxide ions.



A **weak acid** such as ethanoic acid, which is found in vinegar, produces few hydrogen ions when it dissolves in water compared with a strong acid of the same concentration.



The  $\leftrightarrow$  sign means that the reaction is **reversible**. This means that if the ethanoic acid molecule breaks down to give hydrogen ions and ethanoate ions then they will react together to re-form the ethanoic acid molecule. The fact that fewer ethanoic acid molecules dissociate compared with a strong

acid, and that the reaction is reversible, means that few oxonium ions are present in the solution. Other examples of weak acids are citric acid, found in oranges and lemons, carbonic acid, found in soft drinks, sulphurous acid (acid rain) (Figure 7.9) and ascorbic acid (vitamin C).



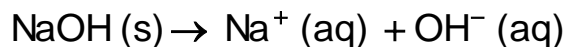
**Figure 7.9** Sulphurous acid is found in acid rain. It is a weak acid and is oxidised to sulphuric acid (a strong acid). Acid rain damages the environment quite badly.

All acids when in aqueous solution produce hydrogen ions,  $\text{H}^+(\text{aq})$ . To say an acid is a strong acid does not mean it is concentrated. The strength of an acid tells you how easily it dissociates (ionises) to produce hydrogen ions. The concentration of an acid indicates the proportions of water and acid present in aqueous solution. It is important to emphasise that a strong acid is still a strong acid even when it is in dilute solution and a weak acid is still a weak acid even if it is concentrated.

### **Strong and weak bases**

An alkali is a base which produces hydroxide ions,  $\text{OH}^-(\text{aq})$ , when dissolved in water. Sodium hydroxide is a **strong alkali** because when it dissolves in water its lattice breaks up completely to produce ions.

sodium hydroxide  $\xrightarrow{\text{water}}$  sodium ions + hydroxide ions



These substances which are strong alkalis produce large quantities of hydroxide ions. Other common, strong soluble bases include potassium hydroxide.

A **weak alkali**, such as ammonia, produces fewer hydroxide ions when it dissolves in water than a strong soluble base of the same concentration.

ammonia + water  $\leftrightarrow$  ammonium ions + hydroxide ions



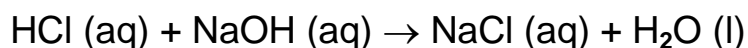
The ammonia molecules react with the water molecules to form ammonium ions and hydroxide ions. However, fewer ammonia molecules do this so only a low concentration of hydroxide ions is produced.

## Neutralising an acid

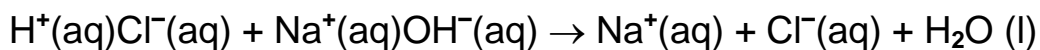
A common situation involving neutralisation of an acid is when you suffer from indigestion. This is caused by a build-up of acid in your stomach. Normally you treat it by taking an indigestion remedy containing a substance which will react with and neutralise the acid.

In the laboratory, if you wish to neutralise a common acid such as hydrochloric acid you can use an alkali such as sodium hydroxide. If the pH of the acid is measured as some sodium hydroxide solution is added to it, the pH increases. If equal volumes of the same concentration of hydrochloric acid and sodium hydroxide are added to one another, the resulting solution is found to have a pH of 7. The acid has been neutralised and a neutral solution has been formed.

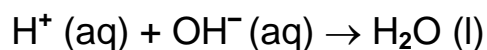
hydrochloric acid + sodium hydroxide  $\rightarrow$  sodium chloride + water



As we have shown, when both hydrochloric acid and sodium hydroxide dissolve in water the ions separate completely. We may therefore write:



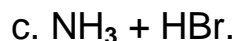
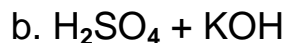
You will notice that certain ions are unchanged on either side of the equation. They are called **spectator ions** and are usually taken out of the equation. The equation now becomes:



This type of equation is known as an ionic equation. The reaction between any acid and alkali in aqueous solution can be summarised by this ionic equation. It shows the ion which causes acidity ( $\text{H}^+(\text{aq})$ ) reacting with the ion which causes alkalinity ( $\text{OH}^- (\text{aq})$ ) to produce neutral water ( $\text{H}_2\text{O} (\text{l})$ ).

## Questions

1. Complete the following equations:



In each case name the acid and the base. Also in parts a and b write the ionic equation for the reactions.

2. Explain the terms 'concentration' and 'strength' as applied to acids.

3. Explain what part water plays in the acidity of a solution.

## Formation of salts

In the example above, sodium chloride was produced as part of the neutralisation reaction. Compounds formed in this way are known as **normal salts**. A normal salt is a compound that has been formed when all the hydrogen ions of an acid have been replaced by metal ions or by the ammonium ion ( $\text{NH}_4^+$ ).

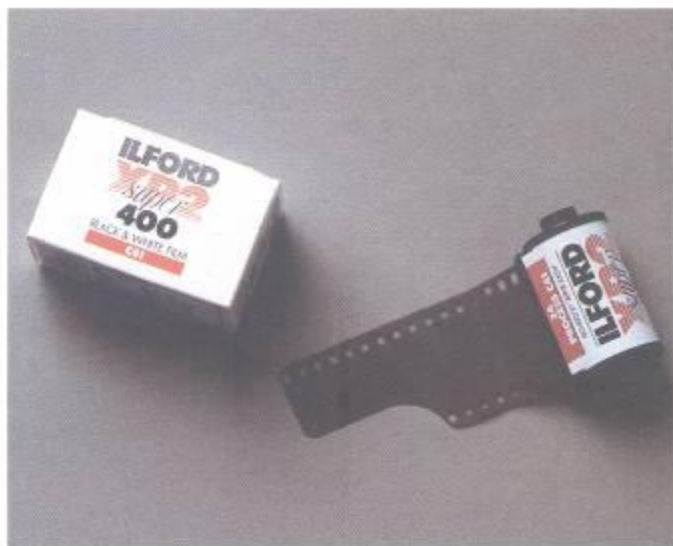
Normal salts can be classified as those which are soluble in water or those which are insoluble in water. The following salts are soluble in cold water:

- all nitrates
- all common sodium, potassium and ammonium salts
- all chlorides except lead, silver and mercury
- all sulphates except lead, barium and calcium.

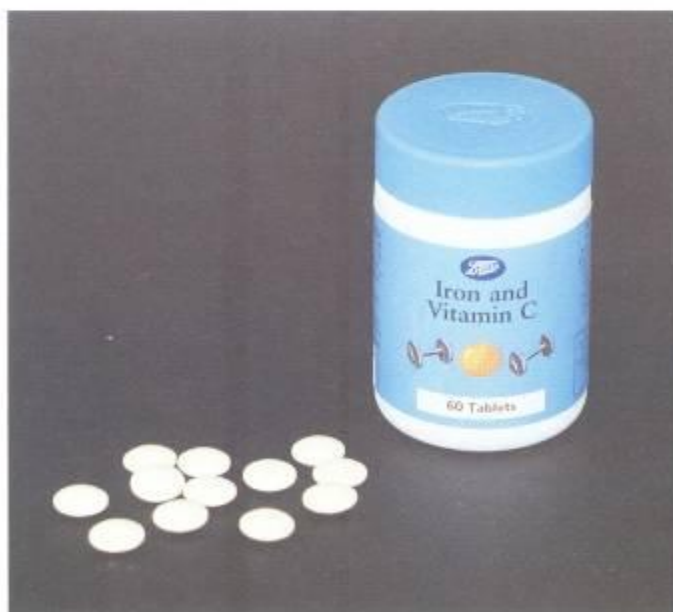
Salts are very useful substances, as you can see from Table 7.2 and Figure 7.10.

Table 7.2 Useful salts.

Salt	Use
Ammonium chloride	In torch batteries
Ammonium sulphate	In fertilisers
Calcium carbonate	Extraction of iron, making cement, glass making
Calcium chloride	In the extraction of sodium, drying agent (anhydrous)
Calcium sulphate	For making plaster boards, plaster casts for injured limbs
Iron (II) sulphate	In 'iron' tablets
Magnesium sulphate	In medicines
Potassium nitrate	In fertiliser and gunpowder manufacture
Silver bromide	In photography
Sodium carbonate	Glass making, softening water, making modern washing powders
Sodium chloride	Making hydrochloric acid, for food flavouring, hospital saline, in the Solvay process for the manufacture of sodium carbonate
Sodium stearate	In some soaps
Tin (II) fluoride	Additive to toothpaste



a Silver bromide is used in photography.



b Iron(II) sulphate is the main substance in these iron and vitamin C tablets.

Figure 7.10 Some uses of salts.

If the acid being neutralised is hydrochloric acid, salts called **chlorides** are formed. Other types of salts can be formed with other acids. A summary of the different types of salt along with the acid they have been formed from is shown in Table 7.3.

Table 7.3 Types of salt and the acids they are formed from.

Acid	Type of salt	Example
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Carbonic acid	Carbonates	Sodium carbonate (Na <sub>2</sub> CO <sub>3</sub> )
Ethanoic acid	Ethanoates	Sodium ethanoate (CH <sub>3</sub> COONa)
Hydrochloric acid	Chlorides	Potassium chloride (KCl)
Nitric acid	Nitrates	Potassium nitrate (KNO <sub>3</sub> )
Sulphuric acid	Sulphates	Sodium sulphate (Na <sub>2</sub> SO <sub>4</sub> )

## Methods of preparing soluble salts

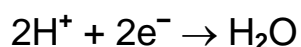
There are four general methods of preparing soluble salts:

### Acid + metal

This method can only be used with the less reactive metals. It would be very dangerous to use a reactive metal such as sodium in this type of reaction. The metals usually used in this method of salt preparation are the **MAZIT** metals, that is, **m**agnesium, **a**luminium, **z**inc, **i**ron and **t**in. A typical experimental method is given below.

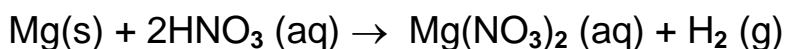
Excess magnesium ribbon is added to dilute nitric acid. During this addition an effervescence is observed due to the production of hydrogen gas. In this reaction the hydrogen ions from the nitric acid gain electrons from the metal atoms as the reaction proceeds.

hydrogen ions + electrons (from metal) → hydrogen gas



How would you test the gas to show that it was hydrogen? What would be the name and formula of the compound produced during the test you suggested?

magnesium + nitric acid → magnesium nitrate + hydrogen



The excess magnesium is removed by filtration (Figure 7.11).

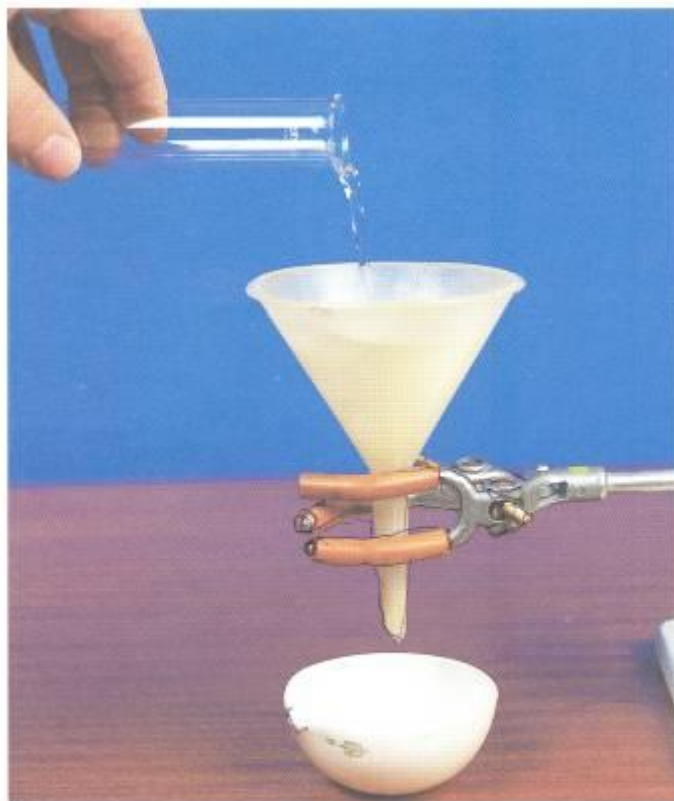


Figure 7.11 The excess magnesium is filtered in this way.

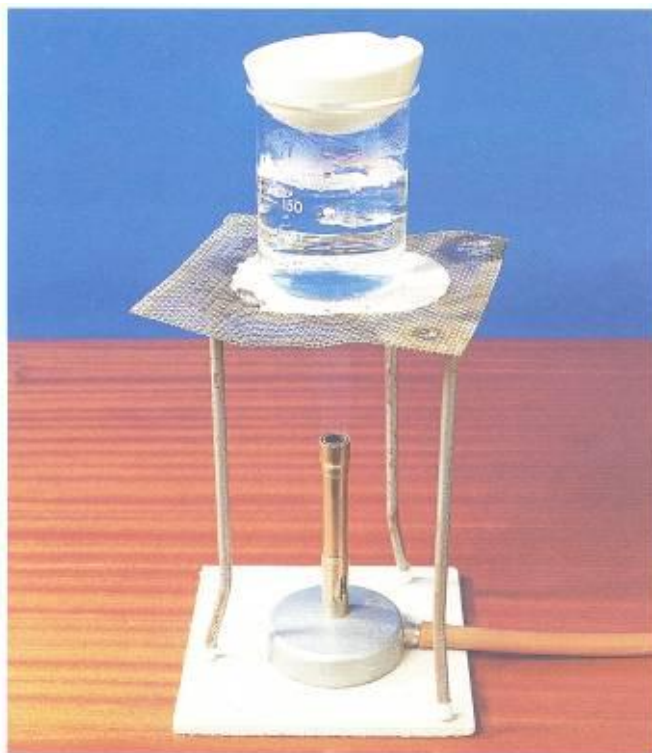


Figure 7.12 The solution of magnesium nitrate is concentrated by slow evaporation.

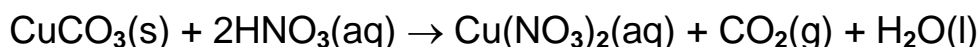
The magnesium nitrate solution is evaporated slowly to form a saturated solution of the salt (Figure 7.12).

The hot concentrated magnesium nitrate solution produced is tested by dipping a cold glass rod into it. If salt crystals form at the end of the rod the solution is ready to crystallise and is left to cool. Any crystals produced on cooling are filtered and dried between clean tissues.

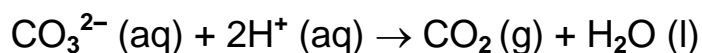
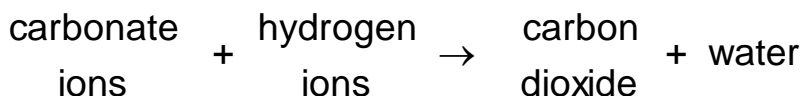
### **Acid + carbonate**

This method can be used with any metal carbonate and any acid, providing the salt produced is soluble. The typical experimental procedure is similar to that carried out for an acid and a metal. For example, copper (II) carbonate would be added in excess to dilute nitric acid. Effervescence would be observed due to the production of carbon dioxide.

How would you test the gas to show it was carbon dioxide? Write an equation to help you explain what is happening during the test you have chosen.



Metal carbonates contain carbonate ions,  $\text{CO}_3^{2-}$ . In this reaction the carbonate ions react with the hydrogen ions in the acid.



### **Acid + alkali (soluble base)**

This method is generally used for preparing the salts of very reactive metals, such as potassium or sodium. It would certainly be too dangerous to add the metal directly to the acid. In this case, we solve the problem indirectly and use an alkali which contains the particular reactive metal

whose salt we wish to prepare.

A **base** is a substance which neutralises an acid, producing a salt and water as the only products. If the base is soluble the term alkali can be used, but there are several bases which are insoluble. In general, most metal oxides and hydroxides (as well as ammonia solution) are bases. Some examples of soluble and insoluble bases are shown in Table 7.4. Salts can be formed by this method only if the base is soluble.

Table 7.4 Examples of soluble and insoluble bases.

Soluble bases (alkalis)	Insoluble bases
Sodium hydroxide (NaOH)	Iron (III) oxide ( $\text{Fe}_2\text{O}_3$ )
Potassium hydroxide (KOH)	Copper (II) oxide (CuO)
Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ )	Lead (II) oxide (PbO)
Ammonia solution ( $\text{NH}_3(\text{aq})$ )	Magnesium oxide (MgO)

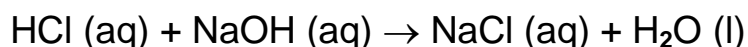
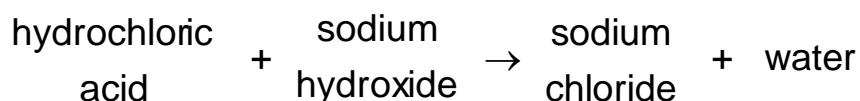
Because in this neutralisation reaction both reactants are in solution, a special technique called titration is required. Acid is slowly and carefully added to a measured volume of alkali using a burette (Figure 7.13) until the indicator, usually phenolphthalein, changes colour.



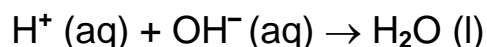
Figure 7.13 The acid is added to the alkali until the indicator just changes colour.

An indicator is used to show when the alkali has been neutralised completely by the acid. This is called the **end-point**. Once you know where the end-point is, you can add the same volume of acid to the measured volume of alkali but this time without the indicator.

The solution which is produced can then be evaporated slowly to obtain the salt. For example,



As previously discussed, this reaction can best be described by the ionic equation:



### **Acid + insoluble base**

This method can be used to prepare a salt of an unreactive metal, such as lead or copper. In these cases it is not possible to use a direct reaction of the metal with an acid so the acid is neutralised using the particular metal oxide (Figure 7.14).



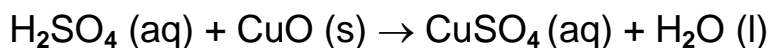
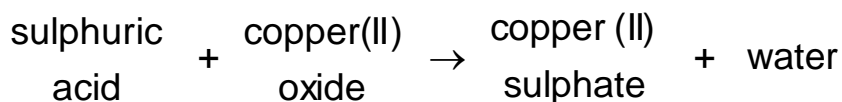
Figure 7.14 The citric acid in the lemon juice reacts with oxide on the surface of the copper and the tarnish dissolves away.

The method is generally the same as that for a metal carbonate and an

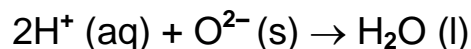
acid, though some warming of the reactants may be necessary. An example of such a reaction is the neutralisation of sulphuric acid by copper (II) oxide to produce copper (II) sulphate (Figure 7.15).



Figure 7.15 After slow evaporation to concentrate the solution, the solution is left to crystallise. Crystals of copper(II) sulphate are produced.

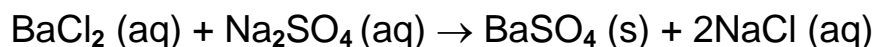
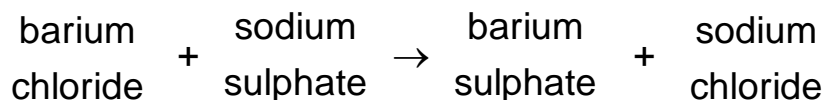


Metal oxides contain the oxide ion,  $\text{O}^{2-}$ . The ionic equation for this reaction is therefore:



### Methods of preparing insoluble salts

An insoluble salt, such as barium sulphate, can be made by precipitation. In this case, solutions of the two chosen soluble salts are mixed (Figure 7.16). To produce barium sulphate, barium chloride and sodium sulphate can be used. The barium sulphate precipitate can be filtered off, washed with distilled water and dried. The reaction that has occurred is:





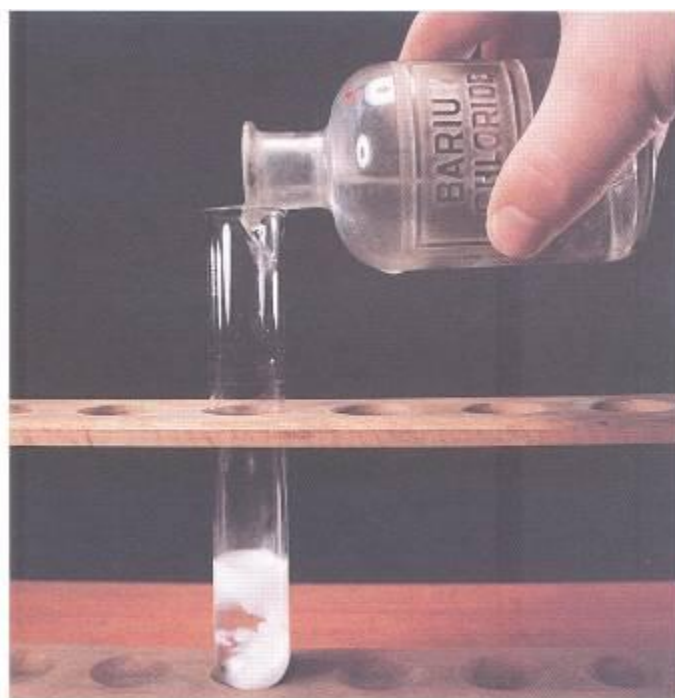
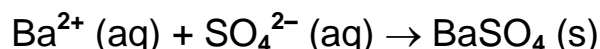
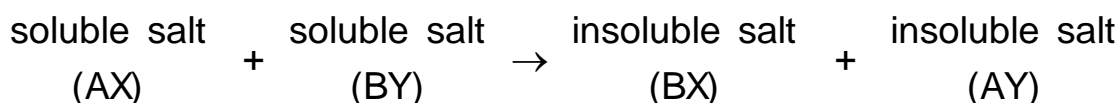


Figure 7.16 When barium chloride solution is added to sodium sulphate a white precipitate of barium sulphate is produced.

The ionic equation for this reaction is:



This method is sometimes known as **double decomposition** and may be summarised as follows



It should be noted that even salts like barium sulphate dissolve to a very small extent. For example, 1 litre of water will dissolve  $2.2 \times 10^{-3}$  g of barium sulphate at 25 °C. This substance and substances like this are said to be **sparingly soluble**.

### More about salts

You have already seen in Table 7.2 that salts are useful substances. Some of the salts shown in that table occur naturally and are mined, for example

calcium sulphate (gypsum) and calcium carbonate (limestone). Many of the others must be made by the chemical industry, for example ammonium nitrate, iron(H) sulphate and silver bromide.

With acids such as sulphuric acid, which has two replaceable hydrogen ions per molecule, it is possible to replace only one of these with a metal ion. The salt produced is called an **acid salt**. An acid salt is one in which not all of the replaceable hydrogen ions of the acid have been replaced by metal ions or the ammonium ion. Some examples of acid salts are shown in Table 7.5.

**Table 7.5 Examples of acid salts.**

<b>Acid</b>	<b>Type of acid salt</b>	<b>Example</b>
Carbonic acid ( $\text{H}_2\text{CO}_3$ )	Hydrogencarbonate	Sodium hydrogencarbonate ( $\text{NaHCO}_3$ )
Sulphuric acid ( $\text{H}_2\text{SO}_4$ )	Hydrogensulphate	Potassium hydrogensulphate ( $\text{KHSO}_4$ )

Sodium hydrogencarbonate is the acid salt used as the raising agent in the baking of cakes and bread, and is often called baking soda (Figure 7.17).



Figure 7.17 Sodium hydrogencarbonate is used as a raising agent.

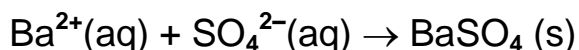
## Testing for different salts

Sometimes we want to analyse a salt and find out what is in it. There are simple chemical tests which allow us to identify the anion part of the salt. These are often called **spot tests**.

## Testing for a sulphate ( $\text{SO}_4^{2-}$ )

You have seen that barium sulphate is a useful insoluble salt. Therefore, if you take a solution of a suspected sulphate and add it to a soluble barium salt (such as barium chloride) then a white precipitate of barium sulphate will be produced.

barium ion + sulphate ion  $\rightarrow$  barium sulphate



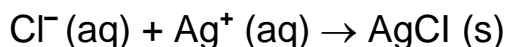
A few drops of dilute hydrochloric acid are also added to this mixture. If the

precipitate does not dissolve, then it is barium sulphate and the unknown salt was in fact a sulphate. If the precipitate does dissolve, then the unknown salt may have been a sulphite (containing the  $\text{SO}_3^{2-}$  ion).

### Testing for a chloride ( $\text{Cl}^-$ ), a bromide ( $\text{Br}^-$ ) or an iodide ( $\text{I}^-$ )

Earlier in this chapter you saw that silver chloride is an insoluble salt. Therefore, if you take a solution of a suspected chloride and add to it a small volume of dilute nitric acid followed by a small amount of a solution of a soluble silver salt (such as silver nitrate) a white precipitate of silver chloride will be produced.

chloride ion + silver ion  $\rightarrow$  silver chloride



If left to stand, the precipitate goes grey (Figure 7.18).



Figure 7.18 If left to stand the white precipitate of silver chloride goes grey. This photochemical change plays an essential part in black and white photography.

In a similar way, a bromide and an iodide will react to produce either a cream precipitate of silver bromide ( $\text{AgBr}$ ) or a yellow precipitate of silver iodide ( $\text{AgI}$ ) (Figure 7.19).

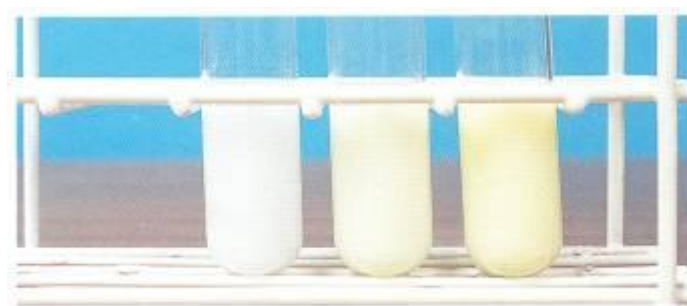
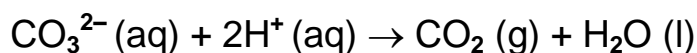


Figure 7.19 AgCl, a white precipitate, AgBr, a cream precipitate, and AgI, a yellow precipitate.

## Testing for a carbonate

If a small amount of an acid is added to some of the suspected carbonate (either solid or in solution) then effervescence occurs. If it is a carbonate then carbon dioxide gas is produced, which will turn limewater 'milky' (a cloudy white precipitate of calcium carbonate forms).

carbonate ions + hydrogen ions  $\rightarrow$  carbon dioxide + water



## Testing for a nitrate

By using Devarda's alloy (45% Al, 5% Zn, 50% Cu) in alkaline solution, nitrates are reduced to ammonia. The ammonia can be identified using damp indicator paper, which turns blue.

## Questions

1. Complete the word equations and write balanced chemical equations for the following soluble salt preparations:

magnesium + sulphuric acid  $\rightarrow$

calcium carbonate + hydrochloric acid  $\rightarrow$

zinc oxide + hydrochloric acid  $\rightarrow$

potassium hydroxide + nitric acid  $\rightarrow$

Also write ionic equations for each of the reactions.

2. Lead carbonate and lead iodide are insoluble. Which two soluble salts could you use in the preparation of each substance? Write

a. a word equation

b. a symbol equation

c. an ionic equation

to represent the reactions taking place.

3. An analytical chemist working for an environmental health organisation has been given a sample of water which is thought to have been contaminated by a sulphate, a carbonate and a chloride.

a. Describe how she could confirm the presence of these three types of salt by simple chemical tests.

b. Write ionic equations to help you explain what is happening during the testing process.



## Crystal hydrates

Some salts, such as sodium chloride, copper carbonate and sodium nitrate, crystallise in their anhydrous forms (without water). However, many salts produce **hydrates** when they crystallise from solution. A hydrate is a salt which incorporates water into its crystal structure. This water is referred to as **water of crystallisation**. The shape of the crystal hydrate is very much dependent on the presence of water of crystallisation. Some examples of crystal hydrates are given in Table 7.6 and shown in Figure 7.20.

Table 7.6 Examples of crystal hydrates.

Salt hydrate	Formula
Cobalt (II) chloride hexahydrate	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$
Copper (II) sulphate pentahydrate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Iron (II) sulphate heptahydrate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Magnesium sulphate heptahydrate	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Sodium carbonate decahydrate	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
Sodium hydrogensulphate monohydrate	$\text{NaHSO}_4 \cdot \text{H}_2\text{O}$
Sodium sulphate decahydrate	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$



Figure 7.20 Hydrate crystals (left to right): cobalt nitrate, calcium nitrate and nickel sulphate (top) and manganese sulphate, copper sulphate and chromium potassium sulphate (bottom).

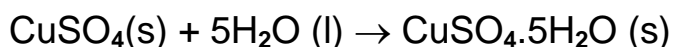
When many hydrates are heated the water of crystallisation is driven away.

For example, if crystals of copper (II) sulphate hydrate (blue) are heated strongly, they lose their water of crystallisation. Anhydrous copper (II) sulphate remains as a white powder:

copper (II) sulphate pentahydrate → anhydrous copper (II) sulphate + water



When water is added to anhydrous copper(II) sulphate the reverse process occurs. It turns blue and the pentahydrate is produced (Figure 7.21). This is an extremely exothermic process.



Because the colour change only takes place in the presence of water, the reaction is used to test for the presence of water.

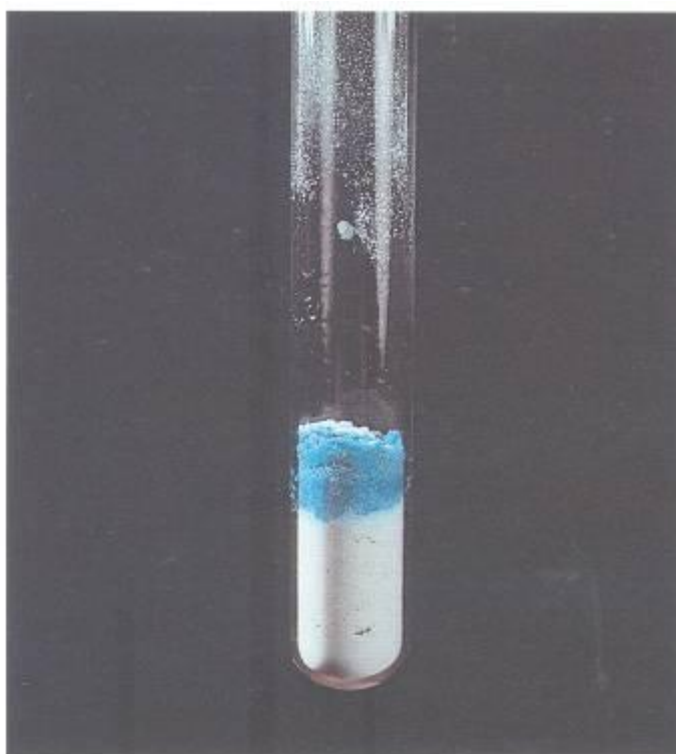


Figure 7.21 Anhydrous copper(II) sulphate is a white powder which turns blue when water is added to it.

Some crystal hydrates **effloresce**, that is they lose some or all of their water of crystallisation to the atmosphere. For example, when colourless

sodium carbonate decahydrate crystals are left out in the air they become coated with a white powder, which is the monohydrate (Figure 7.22). The process is called **efflorescence**.

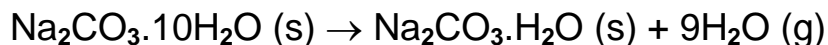


Figure 7.22 A white powder forms on the surface of sodium carbonate decahydrate when it is left in the air.

With some substances, not necessarily salt hydrates, the reverse of efflorescence occurs. For example, if anhydrous calcium chloride is left in the air, it absorbs water vapour and eventually forms a very concentrated solution. This process is called **deliquescence**, and substances which behave like this are said to be **deliquescent**. Solid sodium hydroxide will deliquesce.

There are some substances which, if left out in the atmosphere, absorb moisture but do not change their state. For example, concentrated sulphuric acid, a colourless, viscous liquid, absorbs water vapour from the air and becomes a solution. Substances which do this are said to be **hygroscopic**.

## Calculation of water of crystallisation

Sometimes it is necessary to work out the percentage, by mass, of water of crystallisation in a hydrated salt. The method is the same as that used in Chapter 5, but this time the 'H<sub>2</sub>O' is treated as an element in the calculation.

### Example

Calculate the percentage by mass of water in the salt hydrate  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ . ( $A_r$ : H = 1, O = 16, Mg = 24, S = 32)

$$M_r \text{ for } \text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 24 + 32 + (4 \times 16) + (7 \times 18) \\ = 246$$

The mass of water as a fraction of the total mass of hydrate

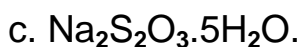
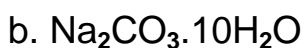
$$= \frac{126}{246}$$

The percentage of water present

$$= \frac{126}{246} \times 100 = 51.2\%$$

## Questions

1. Calculate the percentage by mass of water in the following salt hydrates:



( $A_r$ : H = 1, O = 16, Na = 23, S = 32, Cu = 63.5)

2. Devise an experiment to determine the percentage of water of crystallisation present in a salt hydrate of your choice.

## Solubility of salts in water

Water is a very good solvent and will dissolve a whole range of solutes, including sodium chloride and copper (II) sulphate, as well as other substances such as sugar. You can dissolve more sugar than sodium chloride in 100 cm<sup>3</sup> of water at the same temperature. The sugar is said to be more **soluble** than the sodium chloride at the same temperature. We say that the sugar has a greater **solubility** than the sodium chloride. The solubility of a solute in water at a given temperature is the number of grams of that solute which can be dissolved in 100 g of water to produce a saturated solution at that temperature.

## Calculating solubility

### Example

21.5 g of sodium chloride dissolve in 60 g of water at 25 °C. Calculate the solubility of sodium chloride in water at that temperature.

If 60 g of water dissolves 21.5 g of sodium chloride, then 1 g of water will dissolve:

$$\frac{21.5}{60} \text{ g of sodium chloride}$$

Therefore, 100 g of water will dissolve:

$$\frac{21.5}{60} \times 100 = 35.8 \text{ g}$$

The solubility of sodium chloride at 25°C = 35.8 g per 100 g of water.

## Solubility curves

It is a well-known fact that usually the amount of solute that a solvent will dissolve increases with temperature. We say that the solubility increases with increasing temperature. Figure 7.23 shows how the solubilities of copper (II) sulphate and potassium nitrate vary with temperature. These

graphs of solubility against temperature are known as **solubility curves**. By using curves of this type you can find the solubility of the solute at any temperature.

From a solubility curve such as Figure 7.23, it can be seen that the solubility of potassium nitrate at 50°C is 80 g per 100 g of water, whereas that of copper (II) sulphate is 35 g per 100 g of water.

When a saturated solution is cooled, some of the solute crystallises out of solution. Thus, by using solubility curves it is possible to determine the amount of solute that will crystallise out of solution at different temperatures. For example, if potassium nitrate is cooled from 70°C to 40°C then the difference between the two solubilities at these temperatures tells you the amount that crystallises out.

Solubility at 70°C = 135 g

Solubility at 40°C = 62 g

Difference = 73 g

Therefore the amount of potassium nitrate which crystallises out during cooling from 70 °C to 40°C is 73 g.

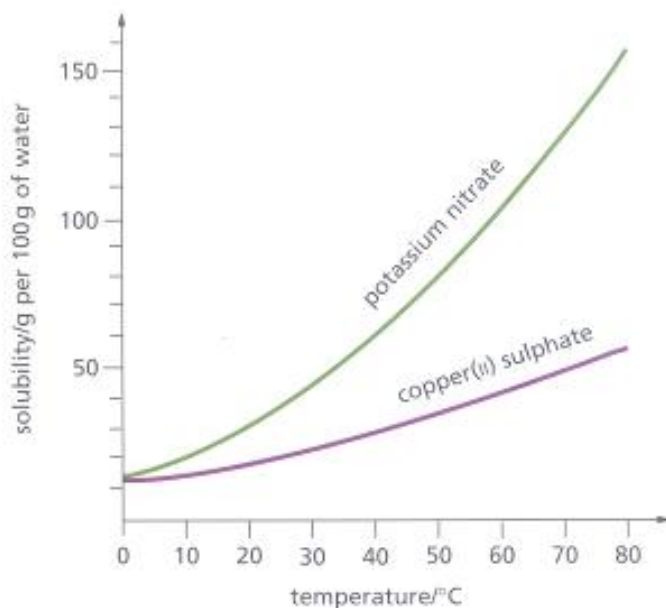


Figure 7.23 Solubility curves for copper(II) sulphate and potassium nitrate.

## Questions

1. Calculate the solubility, at the temperature given, of the following salts in water:

- a. 12.1 g of copper (II) sulphate dissolved in 50 g of water at 30°C
- b. 11.1 g of potassium chlorate (V) dissolved in 60 g of water at 50°C
- c. 9.72 g of potassium chloride dissolved in 30 g of water at 70 °C.

2. Use the data given below to plot a solubility curve for lead nitrate.

Temperature/°C	10	30	50	70	90
Solubility/g per 100 g of water	44.0	60.7	78.6	97.7	117.4

3. Using your solubility curve from question 2, find the solubility of lead nitrate at the following temperatures:

- a. 25°C
- b.. 45°C
- c. 75°C.

4. Using your answers to question 3, calculate the amount of lead nitrate that will crystallise out of solution when cooled from:

- a. 45 °C to 25 °C
- b. 75 °C to 25 °C
- c. 75 °C to 45 °C.

5. 25 g of a saturated solution containing lead nitrate is cooled from 54°C to 27°C. Calculate the amount of lead nitrate that would crystallise out of the solution.



## Titration

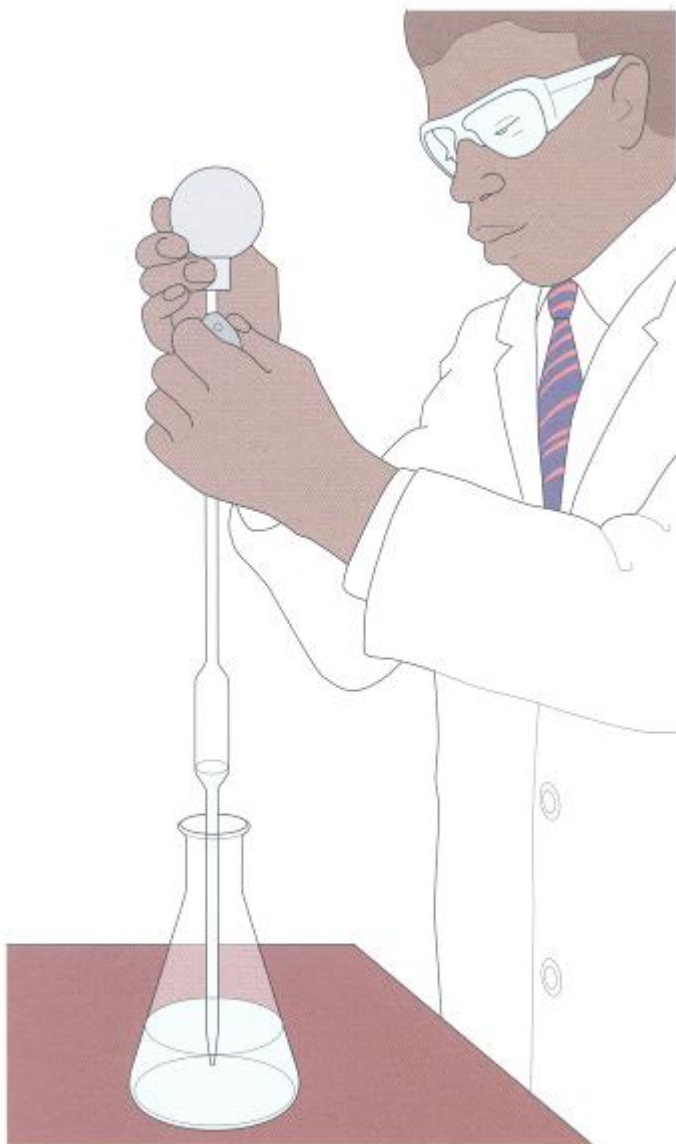


Figure 7.24 Exactly  $25.0\text{ cm}^3$  of sodium hydroxide solution is pipetted into a conical flask.

You saw that it was possible to prepare a soluble salt by reacting an acid with a soluble base (alkali). The method used was that of **titration**. Titration can also be used to find the concentration of the alkali used. In the laboratory, the titration of hydrochloric acid with sodium hydroxide is carried out in the following way.

1.  $25\text{ cm}^3$  of sodium hydroxide solution is pipetted into a conical flask to which a few drops of phenolphthalein indicator have been added (Figure 7.24). Phenolphthalein is pink in alkaline conditions but colourless in acid.
2. A  $0.10\text{ mol}\cdot\text{dm}^{-3}$  solution of hydrochloric acid is placed in the burette using a filter funnel until it is filled up exactly to the zero mark (Figure 7.25).
3. The filter funnel is now removed.

4 The hydrochloric acid is added to the sodium hydroxide solution in small quantities — usually no more than  $0.5\text{ cm}^3$  at a time (Figure 7.26). The contents of the flask must be swirled after each addition of acid for thorough mixing.

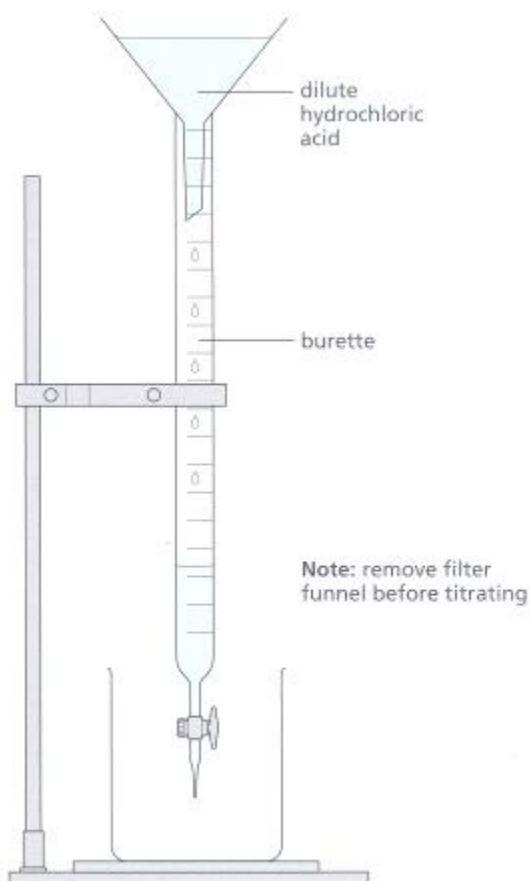


Figure 7.25 The burette is filled up to the zero mark with a  $0.10 \text{ mol dm}^{-3}$  solution of hydrochloric acid.

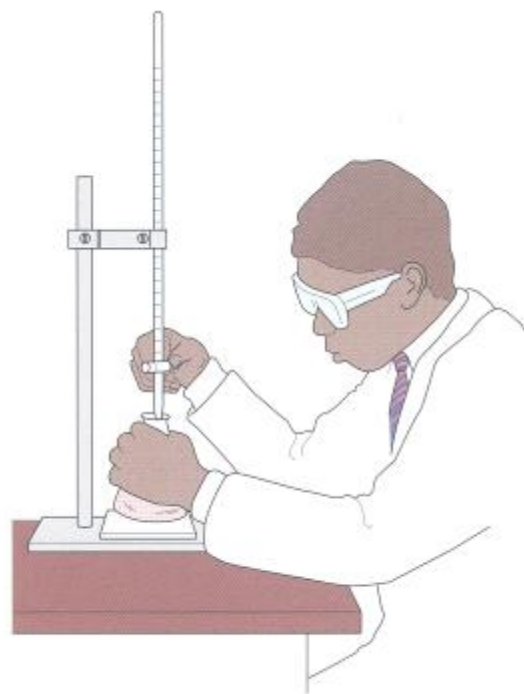


Figure 7.26 The titration is carried out accurately.

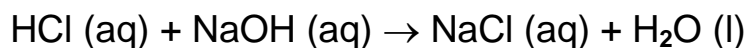
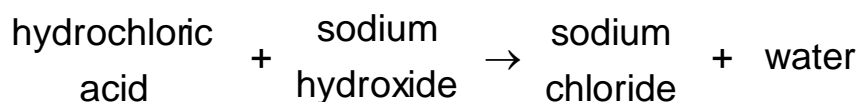
5. The acid is added until the alkali has been neutralised completely. This is shown by the pink colour of the indicator just disappearing.

6. The final reading on the burette at the end-point is recorded and further titrations carried out until consistent results are obtained (within  $0.1 \text{ cm}^3$  of each other). Some sample data are shown below.

Volume of sodium hydroxide solution  
=  $25.0 \text{ cm}^3$

Average volume of  $0.10 \text{ mol dm}^{-3}$  solution of hydrochloric acid added  
=  $21.0 \text{ cm}^3$

The neutralisation reaction which has taken place is:



From this equation it can be seen that 1 mole of hydrochloric acid neutralises 1 mole of sodium hydroxide.

Now you can work out the number of moles of the acid using the formula given in Chapter 5.

$$\text{moles} = \frac{\text{volume}}{1000} \times \text{concentration}$$

$$= \frac{21.0 \times 0.10}{1000}$$

$$= 2.1 \times 10^{-3}$$

$$\begin{array}{ccc} \text{number of moles} & & \text{number of moles} \\ \text{of hydrochloric acid} & = & \text{of sodium hydroxide} \end{array}$$

Therefore, the number of moles of sodium hydroxide =  $2.1 \times 10^{-3}$

$2.1 \times 10^{-3}$  moles of sodium hydroxide is present in  $25.0 \text{ cm}^3$  of solution.

Therefore, in  $1 \text{ cm}^3$  of sodium hydroxide solution we have

$$\frac{2.1 \times 10^{-3}}{25.0} \text{ moles}$$

Therefore, in 1 litre of sodium hydroxide solution we have

$$\frac{2.1 \times 10^{-3}}{25.0} \times 1000 = 0.084 \text{ mole}$$

The concentration of sodium hydroxide solution is  $0.084 \text{ mol}\cdot\text{dm}^{-3}$  (0.084 M).

You can simplify the calculation by substituting in the following mathematical equation:

$$\frac{M_1 V_1}{M_{\text{acid}}} = \frac{M_2 V_2}{M_{\text{alkali}}}$$

where:

$M_1$  = molarity (concentration) of the acid used

$V_1$  = volume of acid used ( $\text{cm}^3$ )

$M_{\text{acid}}$  = number of moles of acid shown in the chemical equation

$M_2$  = molarity (concentration) of the alkali used

$V_2$  = volume of the alkali used ( $\text{cm}^3$ )

$M_{\text{alkali}}$  = number of moles of alkali shown in the chemical equation

In the example:

$M_1 = 0.10 \text{ mol}\cdot\text{dm}^{-3}$

$V_1 = 21.0 \text{ cm}^3$

$M_{\text{acid}} = 1 \text{ mole}$

$M_2 = \text{unknown}$

$V_2 = 25.0 \text{ cm}^3$

$M_{\text{alkali}} = 1 \text{ mole}$

Substituting in the equation:

$$\frac{0.10 \times 21.0}{1} = \frac{M_2 \times 25.0}{1}$$

Rearranging:

$$M_2 = \frac{0.10 \times 21.0 \times 1}{1 \times 25.0}$$

$$M_2 = 0.084$$

The molarity of the sodium hydroxide solution = 0.084 M. It is a solution of concentration 0.084 mol·dm<sup>-3</sup>.

## Questions

1. 24.2 cm<sup>3</sup> of a solution containing 0.20 mol·dm<sup>-3</sup> of hydrochloric acid just neutralised 25.0 cm<sup>3</sup> of a potassium hydroxide solution. What is the concentration of this potassium hydroxide solution?
2. 22.4 cm<sup>3</sup> of a solution containing 0.10 mol·dm<sup>-3</sup> of sulphuric acid just neutralised 25.0 cm<sup>3</sup> of a sodium hydroxide solution. What is the concentration of this sodium hydroxide solution?

## Checklist

After studying Chapter 7 you should know and understand the following terms.

**Acid** A substance which dissolves in water, producing  $\text{H}^+(\text{aq})$  ions as the only positive ions.

**Acid salt** A substance formed when only some of the replaceable hydrogen of an acid is replaced by metal ions or the ammonium ion ( $\text{NH}_4^+$ )

**Alkali** A soluble base which produces  $\text{OH}^-(\text{aq})$  ions in water.

**Base** A substance which neutralises an acid, producing a salt and water as the only products.

**Deliquescence** The process during which a substance absorbs water vapour from the atmosphere and eventually forms a very concentrated solution.

**Double decomposition** The process by which an insoluble salt is prepared from solutions of two suitable soluble salts.

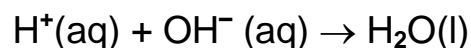
**Efflorescence** The process during which a substance loses water of crystallisation to the atmosphere.

**Hygroscopic** The ability to absorb water vapour from the atmosphere without forming solutions or changing state, for example concentrated sulphuric acid.

**Indicator** A substance used to show whether a substance is acidic or alkaline (basic), for example phenolphthalein.

**Ionic equation** The simplified equation of a reaction which we can write if the chemicals involved are ionic substances.

**Neutralisation** The process in which the acidity or alkalinity of a substance is destroyed. Destroying acidity means removing  $\text{H}^+(\text{aq})$  by reaction with a base, carbonate or metal. Destroying alkalinity means removing the  $\text{OH}^-(\text{aq})$  by reaction with an acid.



**Normal salt** A substance formed when all the replaceable hydrogen of an acid is completely replaced by metal ions or the ammonium ion ( $\text{NH}_4$ ).

**pH scale** A scale running from 0 to 14, used for expressing the acidity or alkalinity of a solution.

**Salt hydrates** Salts containing water of crystallisation.

**Solubility** The solubility of a solute in a solvent at a given temperature is the number of grams of that solute which can dissolve in 100 g of solvent to produce a saturated solution at that temperature.

**Solubility curve** This is a graph of solubility against temperature.

**Strong acid** One which produces a high concentration of  $\text{H}^+(\text{aq})$  ions in water solution, for example hydrochloric acid.

**Strong alkali** One which produces a high concentration of  $\text{OH}^-(\text{aq})$  ions in water solution, for example sodium hydroxide.

**Testing for a carbonate** If effervescence occurs when an acid is added to the suspected carbonate and the gas produced tests positively for carbon dioxide, the substance is a carbonate.

**Testing for a chloride** If a white precipitate is produced when dilute nitric acid and silver nitrate solution are added to the suspected chloride, the solution contains a chloride.

**Testing for a sulphate** If a white precipitate is produced when dilute hydrochloric acid and barium chloride solution are added to the suspected sulphate, the solution contains a sulphate.

**Titration** A method of volumetric analysis in which a volume of one reagent (for example an acid) is added to a known volume of another reagent (for example an alkali) slowly from a burette until an end-point is reached. If an acid and alkali are used, then an indicator is used to show that the end-point has been reached.



**Water of crystallisation** Water incorporated into the structure of substances as they crystallise, for example copper (II) sulphate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ).

**Weak acid** One which produces a low concentration of  $\text{H}^+$  (aq) in water solution, for example ethanoic acid.

**Weak alkali** One which produces a low concentration of  $\text{OH}^-$  (aq) in water solution, for example ammonia solution.

## **Acids, Bases, and Salts**

### **Additional questions**

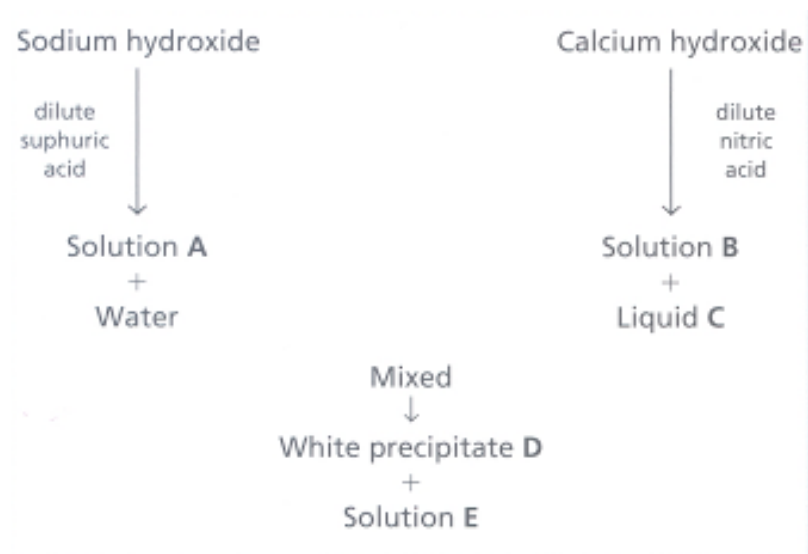
1. Describe briefly the contribution to the theory of acids and bases by:
  - a. Antoine Lavoisier (1743–1794)
  - b. Sir Humphry Davy (1778–1829)
  - c. Justus von Liebig (1803–1873)
  - d. Svante Arrhenius (1859–1927)
  - e. Johannes Brønsted (1879–1947) and Thomas Lowry (1874–1936).

2a. Copy out and complete the table, which covers the different methods of preparing salts.

Method of preparation	Name of salt prepared	Two substances used in the preparation
Acid + alkali	Potassium sulphate	..... and .....
Acid + metal	.....	.....and dilute hydrochloric acid
Acid + insoluble base	Magnesium sulphate	..... and .....
Acid + carbonate	Copper.....	..... and .....
Precipitation	Lead iodide	..... and .....

b. Write word and balanced chemical equations for each reaction shown in your table. Also write ionic equations where appropriate.

3. Study the following scheme.



- Give the names and formulae of substances A to E.
- Describe a test which could be used to identify the presence of water.
- Which indicator is suitable for the initial reaction between the hydroxides and the dilute acids shown?
- Write balanced chemical equations for the reactions taking place in the scheme.
- Write an ionic equation for the production of the white precipitate D.

4. In a titration involving  $24.0 \text{ cm}^3$  potassium hydroxide solution against a solution containing  $1 \text{ mol}\cdot\text{dm}^{-3}$  of sulphuric acid,  $28.0 \text{ cm}^3$  of the acid was found to just neutralise the alkali completely.

- a. Write a word and balanced chemical equation for the reaction.
- b. Name a suitable indicator for the titration and state the colour change you would observe.
- c. Calculate the concentration of the alkali in  $\text{mol}\cdot\text{dm}^{-3}$ .
- d. Describe a chemical test which you could use to identify the type of salt produced during the reaction.

5. Explain the following, with the aid of examples:

a. neutralisation

b. titration

c. soluble salt

d. insoluble salt.

6. Ammonium nitrate is used in fertilisers. The table below shows the solubility of this substance in water at various temperatures.

Temperature/°C	0	10	20	30	40	50	60	70
Solubility/g per 100 g H <sub>2</sub> O	28	36	44	52	60	70	82	96

a. Plot these results as a solubility curve for ammonium nitrate.

b. Use your graph to answer the following questions.

(i) What is the solubility of ammonium nitrate at 8°C, 27°C, 45°C and 66°C?

(ii) Using your answers to (i), calculate the amount of ammonium nitrate that will crystallise out of solution when it is cooled from 45°C to 8°C.

(iii) Calculate the amount of ammonium nitrate which would crystallise out of solution if 20 g of saturated solution was cooled from 63°C to 28°C.



7. Read the following passage and then answer the questions which follow.

Sodium carbonate decahydrate effloresces quite readily. With some substances, such as solid sodium hydroxide, the reverse of efflorescence occurs - they deliquesce. There are some substances, such as concentrated sulphuric acid, which when left open to the atmosphere are diluted - they are hygroscopic.

- a. What are the meanings of the terms in italics?
- b. What precautions should be taken to ensure that these substances are not involved in the processes described above?
- c. Which of the other salts shown in Table 7.6 are likely to effloresce? Give a reason for your answer.

8. Copper (II) sulphate crystals exist as the pentahydrate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . It is a salt hydrate. If it is heated quite strongly, the water of crystallisation is driven off and the anhydrous salt remains.

a. Explain the meaning of the terms shown in *italics*.

b. Describe the experiment you would carry out to collect a sample of the water given off when the salt hydrate was heated strongly. Your description should include a diagram of the apparatus used and a chemical equation to represent the process taking place.

c. Describe a chemical test you could carry out to show that the colourless liquid given off was water.

d. Describe one other test you could carry out to show that the colourless liquid obtained in this experiment was pure water.

e. Sometimes it is necessary to work out the percentage by mass of water of crystallisation as well as the number of moles of water present in a hydrated crystal.

(i) Use the information given below to calculate the percentage, by mass, of water of crystallisation in a sample of hydrated magnesium sulphate.

Mass of crucible	= 14.20 g
Mass of crucible + hydrated $\text{MgSO}_4$	= 16.66g
Mass after heating	= 15.40 g

(ii) Calculate the number of moles of water of crystallisation driven off during the experiment as well as the number of moles of anhydrous salt remaining. ( $A_r$ : H = 1; O = 16; Mg = 24; S = 32)

(iii) Using the information you have obtained in (ii), write down, in the form  $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$ , the formula of hydrated magnesium sulphate.